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Highly selective fluoride sensing via chromogenic aggregation of a silyloxy-functionalized tetraphenylethylene (TPE) derivative

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ABSTRACT

A silyloxy-functionalized tetraphenylethylene (TPE) derivative shows a remarkable change in the absorption spectrum on deprotection with fluoride ions. The reaction process is highly selective for fluoride and the resulting charge transfer band results in a bright green solution. A simple selective visual assay of aqueous fluoride ions was also obtained by the impregnation of cellulose strips with the TPE derivative.

Tetraphenylethylene (TPE) and its derivatives have attracted remarkable attention due to their well-known aggregation-induced emission (AIE)[1] properties, which make this small molecule an indispensible building block in several areas such as OLEDs, chemosensors, and bioprobes.[2] The outstanding electrochemical, physical, and excited state properties, especially in the solid state, are a result of the extended π-system found in TPE.[3]

Fluoride ion sensing is an important topic because of the biological significance of this anion, especially in relation to dental care, and in the treatment of osteoporosis.[4] However, fluoride ion sensing is a highly challenging task due to the high electronegativity of fluorine, its strong hydrogen bonding ability and its size (smallest anion).

In addition, real time monitoring of fluoride ions is extremely difficult in aqueous media, especially via chromogenic chemosensors due to competitive hydrogen bonding between fluoride and water molecules.[5] A reaction-based sensor could have some advantages considering the simplicity of the analytical procedure. In this respect, naked eye anion detection with chemosensors capable of detecting anions is becoming increasingly important for rapid on-site analysis, on a real time basis. Current chromogenic anion sensors typically have hydrogen bonding receptor sites, some with selectivity for fluoride, but are less likely to work in aqueous medium.[6]

The high chemical affinity between fluoride and silicon has been widely used in previous studies to sense fluoride anions, however, there are only a few which work in aqueous solutions.[7]

Herein, we report the design and synthesis of a highly selective and sensitive chromogenic fluoride anion sensor, TPE **5**. The synthesis of target compound **5** started with the reaction between 4-methoxyphenyllithium (from 1-bromo-4-methoxybenzene and butyllithium) and 4-methoxybenzaldehyde to produce alcohol **1**, which was oxidized to compound **2** using manganese(IV) oxide in dichloromethane. Compound **3** was then obtained through a McMurry coupling of compound **2**. This was followed by demethylation to give **4**. Further reaction of compound **4** with chlorotriisopropylsilane in the presence of imidazole yielded the target fluoride anion sensor **5** (Scheme 1).

Fluoride sensing of TPE **5** was accomplished by deprotection of the silyl groups from the TPE core generating four phenoxide ions in full conjugation with the TPE moiety, which leads to very strong intramolecular charge transfer (ICT).[8]

This strong ICT resulted not only in the formation of new charge transfer bands in the absorbance spectrum corresponding to a bright green solution, but also led to quenching of the emission in the fluorescence spectrum.

In the electronic absorption spectrum, a maximum was observed at 340 nm for compound **5** in DMF. Next, the solution of compound **5** (50 μM in DMF) was treated with fluoride ions in the form of a tetrabutylammonium salt (TBAF). The absorption spectra during titration showed new bands appearing at 452, 510, 600 and 680 nm, respectively. The band at 600 nm was the

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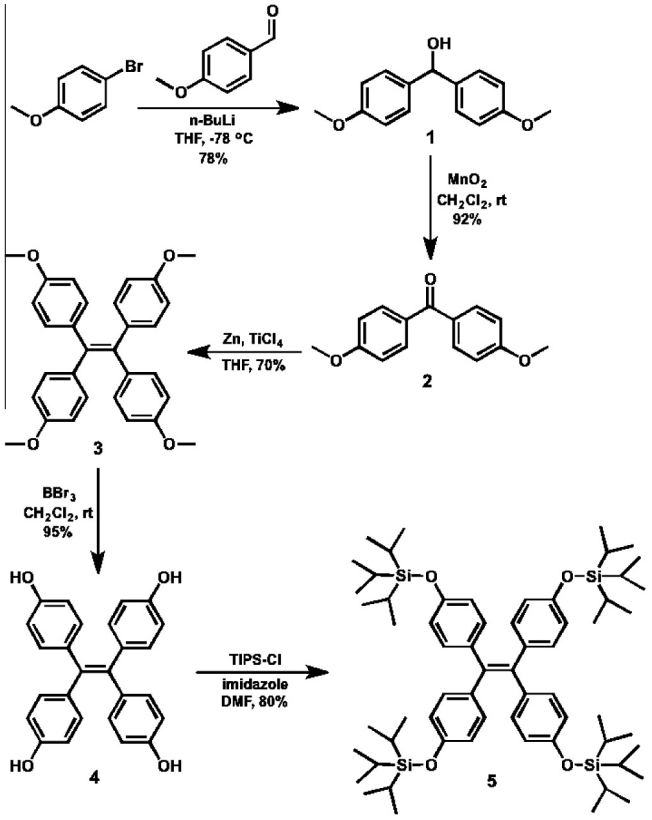

Scheme 1. Synthesis of fluoride sensor **5**.

most intense, resulting in a bright green color of the solution (Fig. 1).

The electronic absorption spectra of **5** were also investigated upon the addition of eight equivalents of the TBA salts of HSO_4^-, $H_2PO_4^-$, AcO^-, NO_3^-, CN^-, I^-, Br^-, and Cl^- to DMF solutions of **5**. The addition of these anions did not result in any changes in the absorption spectrum (Fig. S1), or the emission spectrum.

Figure 2 (bottom) shows the color change after the addition of eight equivalents of the anions as TBA salts to the DMF solution of **5**. Clearly, no color change was observed upon addition of the other anions; only fluoride ions led to a color change.

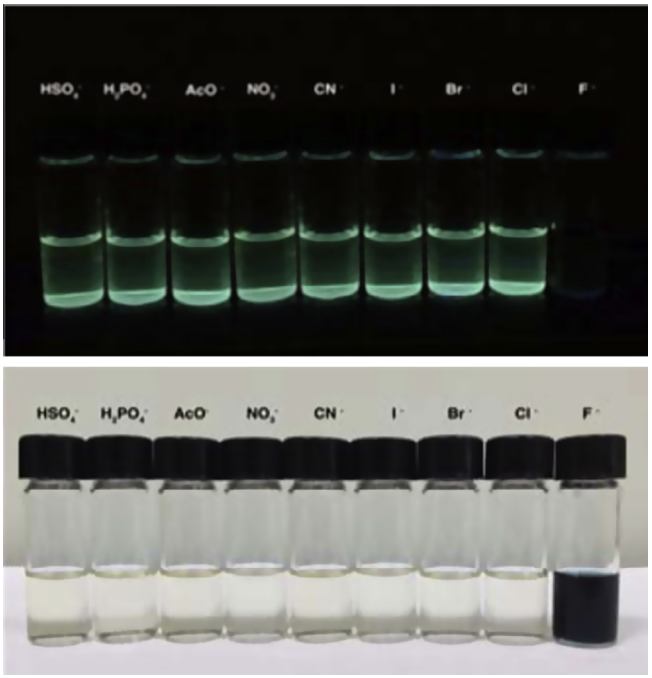

Figure 2. The digital photographs show the appearance of the solutions under a hand-held UV lamp (360 nm) (top) and under ambient light (bottom). Probe concentrations were 50 μM and the anions were added at 0.4 mM concentrations, all in DMF.

The emission spectra of compound **5** (50 μM in DMF) showed drastic quenching upon addition of fluoride anions in the form of TBA salts (Fig. 3). The strong charge transfer character of the formed phenoxide moieties leads to this quenching. As expected, no emission quenching was observed upon addition of other ions as TBA salts as shown in Figure 4 (top). The spectacular difference between fluoride anions and the other anions in terms of emission intensity is clearly shown in the bar graphs (Fig. 4, bottom). Furthermore, selective quenching of fluoride is shown in the digital photographs of DMF solutions under the indicated conditions (Fig. 2, top).

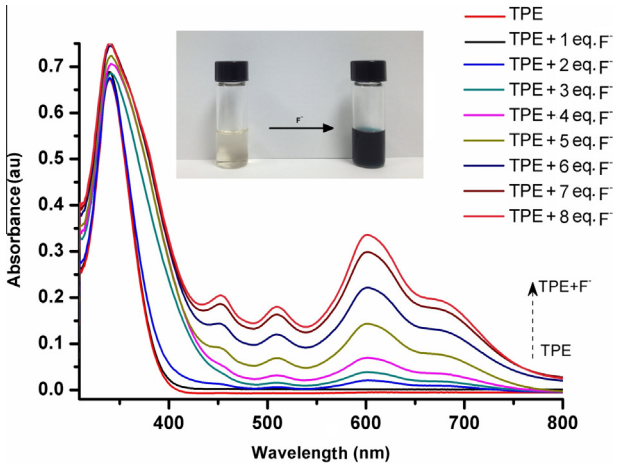

Figure 1. Absorbance spectra of compound **5** + F^- in the presence of increasing F^- concentrations. The inset is a digital photograph of the probe (left) and probe following the addition of 8 equivalents of F^- (right). Probe concentration is 50 μM in DMF.

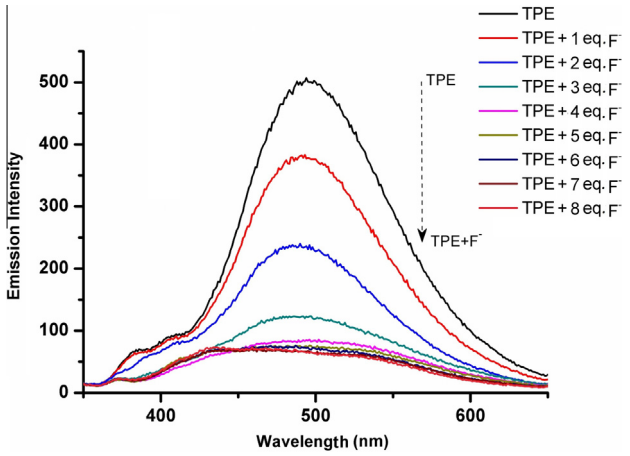

Figure 3. Emission spectra of compound **5** + F^- in the presence of increasing F^- concentrations. Probe concentration is 50 μM in DMF. Excitation wavelength is 340 nm.

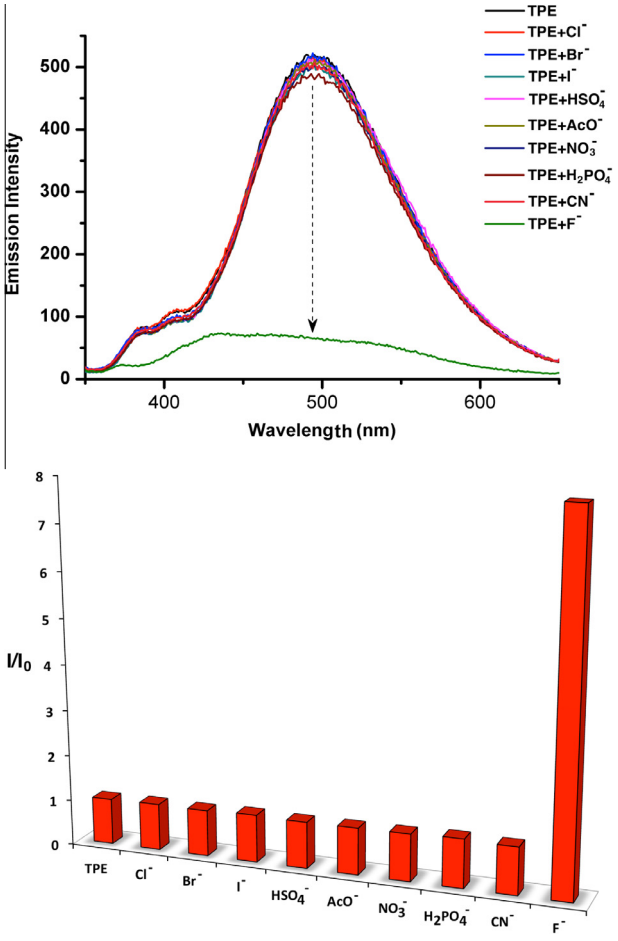

Figure 4. Emission spectra of compound **5** upon the addition of 8 equivalents of Cl^-, Br^-, I^-, HSO_4^-, AcO^-, NO_3^-, $H_2PO_4^-$, and CN^-. The F^- and probe concentrations are both 50 μM, all in DMF. The bar graph shows the emission ratios (I/I_o).

In order to explore whether compound **5** could respond to fluoride anions in solid state via chemical reactions, we decided to prepare a test paper for detecting fluoride in an aqueous environment by dipping a cellulose strip (3.0×0.5 cm^2) into a tetrahydrofuran solution of **5** (4.0 mM). After drying the cellulose strip under ambient conditions, it was immersed in an aqueous fluoride solution (water/tetrahydrofuran, 2:8) for several seconds followed by a short heat treatment.

The color of the cellulose strip was clearly and reproducibly changed from white to green (Fig. 5). However the color change was not uniform throughout the test strip. The underlying reason for this maybe that the sensing process was achieved by a chemical reaction taking place on the cellulose fibers, introducing some heterogeneity in the solid state.

In conclusion, we have reported a new chemical reaction based on a chromogenic fluoride anion probe operating via deprotection of the silyl groups from TPE derivative **5**. The deprotection of four silyl groups results in four donor phenoxide groups causing strong intramolecular charge transfer. This strong ICT also induces considerable fluorescence quenching and the occurrence of new absorbance bands in the visible region resulting in a bright green solution. This highly selective sensing was also, demonstrated in aqueous environments using a stained cellulose strip. Thus, a naked-eye chromogenic chemosensor **5** has been described for detection of fluoride anions and this dye impregnated cellulose strip could be a prototype material for the easy and fast chemical detection of fluoride.

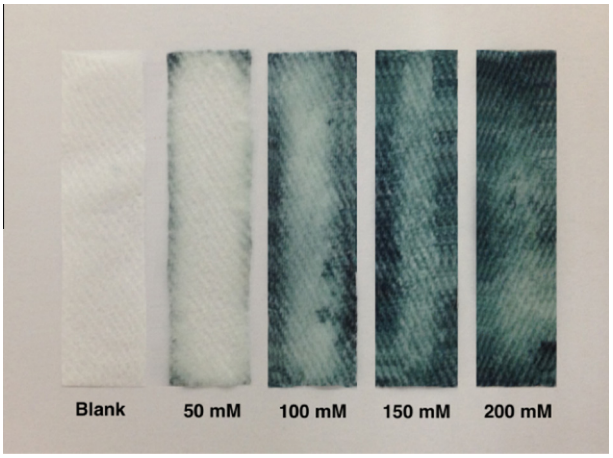

Figure 5. The color changes of the treated cellulose strips prepared for the detection of fluoride anions in aqueous environments, on exposure to different fluoride concentrations.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.11.059.

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